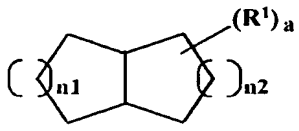
CLAIMS

1. An immersion exposure liquid used for an immersion exposure device or an immersion exposure method in which a substrate is exposed through a liquid provided between a lens of a projection optical system and the substrate, the immersion exposure liquid being liquid in an operating temperature range of the immersion exposure device and comprising an alicyclic hydrocarbon compound or a cyclic hydrocarbon compound containing a silicon atom in its ring structure.

2. The immersion exposure liquid according to claim 1, wherein the alicyclic hydrocarbon compound or the cyclic hydrocarbon compound containing a silicon atom in its ring structure has a transmittance of radiation with a wavelength of 193 nm of 70% or more at an optical path length of 1 mm and has a refractive index for D lines of 1.4 or more.

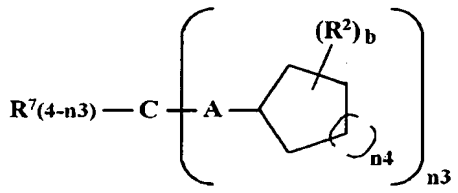
3. The immersion exposure liquid according to claim 2, wherein the alicyclic hydrocarbon compound or the cyclic hydrocarbon compound containing a silicon atom in its ring structure is at least one compound selected from compounds of the following formulas (1-1) to (1-9),



(1-1)

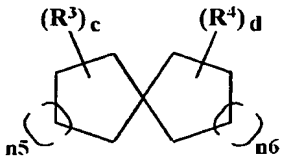
wherein R^1 represents an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a cyano group, a hydroxyl group, a fluorine atom, a fluorine-substituted hydrocarbon group having 1 to 10 carbon atoms, a group $-Si(R^9)_3$, or a group $-SO_3R^{10}$, n1 and n2 individually represent integers

from 1 to 3, a represents an integer from 0 to 10, provided that, when two or more R^1s exist, the R^1s may be the same or different, and two or more R^1s may be bonded to form a ring structure, and R^9 and R^{10} represent alkyl groups having 1 to 10 carbon atoms,



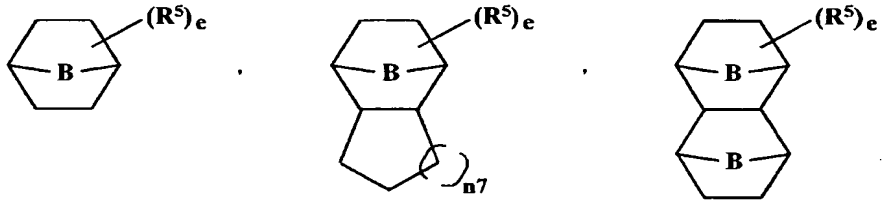
(1-2)

wherein A represents a single bond, a methylene group which may be replaced with an alkyl group having 1 to 10 carbon atoms, or an alkylene group having 2 to 14 carbon atoms which may be replaced with an alkyl group having 1 to 10 carbon atoms, R^2 represents an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a cyano group, a hydroxyl group, a fluorine atom, a fluorine-substituted hydrocarbon group having 1 to 10 carbon atoms, a group $-Si(R^9)_3$, or a group $-SO_3R^{10}$, R^7 represents a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, a cyano group, a hydroxyl group, a fluorine atom, a fluorine-substituted alkyl group having 1 to 10 carbon atoms, or a group $-Si(R^9)_3$, provided that, when two or more R^7s exist, the R^7s may be the same or different, and two or more R^7s may be bonded to form a ring structure, n3 represents an integer from 2 to 4, n4 represents an integer from 1 to 3, b represents an integer from 0 to 6, provided that, when two or more R^2s exist, the R^2s may be the same or different, and two or more R^2s may be bonded to form a ring structure, and R^9 and R^{10} represent alkyl groups having 1 to 10 carbon atoms,



(1-3)

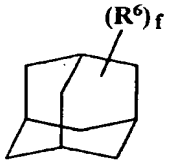
wherein R^3 and R^4 represent an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a cyano group, a hydroxyl group, a fluorine atom, a fluorine-substituted hydrocarbon group having 1 to 10 carbon atoms, a group $-Si(R^9)_3$, or a group $-SO_3R^{10}$, provided that, when two or more R^3s and R^4s exist, the R^3s and the R^4s may be respectively the same or different, and two or more R^3s and R^4s may respectively form ring structures or may be bonded to form a ring structure, n5 and n6 represent integers from 1 to 3, c and d represent integers from 0 to 8, and R^9 and R^{10} represent alkyl groups having 1 to 10 carbon atoms,



(a) (b) (c)

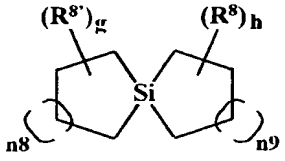
(1-4)

wherein B represents a methylene group or an ethylene group, R^5 represents an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a cyano group, a hydroxyl group, a fluorine atom, a fluorine-substituted hydrocarbon group having 1 to 10 carbon atoms, a group $-Si(R^9)_3$, or a group $-SO_3R^{10}$, e represents an integer from 0 to 10, n7 represents an integer from 1 to 3, provided that, when two or more R^5s exist, the R^5s may be the same or different, and two or more R^5s may be bonded to form a ring structure, and R^9 and R^{10} represent alkyl groups having 1 to 10 carbon atoms,



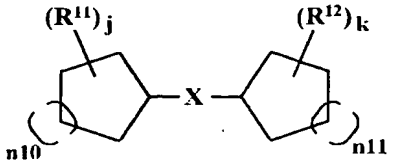
(1-5)

wherein R^6 represents an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a cyano group, a hydroxyl group, a fluorine atom, a fluorine-substituted hydrocarbon group having 1 to 10 carbon atoms, a group $-Si(R^9)_3$, or a group $-SO_3R^{10}$, f represents an integer from 0 to 10, provided that, when two or more R^6s exist, the R^6s may be the same or different, and R^9 and R^{10} represent alkyl groups having 1 to 10 carbon atoms,



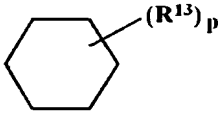
(1-6)

wherein R^8 and $R^{8'}$ represent an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a cyano group, a hydroxyl group, a fluorine atom, a fluorine-substituted hydrocarbon group having 1 to 10 carbon atoms, a group $-Si(R^9)_3$, or a group $-SO_3R^{10}$, g and h individually represent integers from 0 to 6, n8 and n9 represent integers from 1 to 3, and R^9 and R^{10} represent alkyl groups having 1 to 10 carbon atoms,



(1-7)

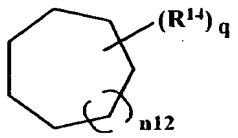
wherein R^{11} and R^{12} represent an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a cyano group, a hydroxyl group, a fluorine atom, a fluorine-substituted hydrocarbon group having 1 to 10 carbon atoms, a group $-Si(R^9)_3$, or a group $-SO_3R^{10}$, n10 and n11 individually represent integers from 1 to 3, j and k represent integers from 0 to 6, provided that, when two or more R^{11}s and R^{12}s exist, the R^{11}s and the R^{12}s may be the same or different, and two or more R^{11}s may be bonded to form a ring structure or two or more R^{12}s may be bonded to form a ring structure, X represents a single bond, a divalent aliphatic hydrocarbon group having 2 to 10 carbon atoms, or a divalent alicyclic hydrocarbon group having 3 to 14 carbon atoms, and R^9 and R^{10} represent alkyl groups having 1 to 10 carbon atoms,



(1-8)

wherein R^{13} represents an alkyl group having two or more carbon atoms, an alicyclic hydrocarbon group having three or more carbon atoms, a cyano group, a hydroxyl group, a fluorine atom, a fluorine-substituted hydrocarbon group having 2 to 10 carbon atoms, a group $-Si(R^9)_3$, or a group $-SO_3R^{10}$, p represents an integer from 1 to 6, provided that, when two or more R^{13}s exist, the R^{13}s may be the same or different, and two or more R^{13}s may be bonded to form a ring structure, and R^9 and R^{10} represent alkyl groups

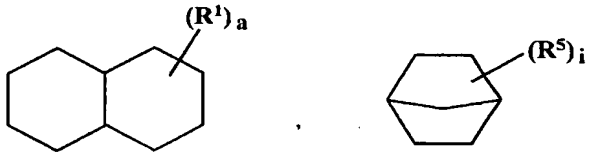
having 1 to 10 carbon atoms,



(1-9)

wherein R^{14} represents an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a cyano group, a hydroxyl group, a fluorine atom, a fluorine-substituted hydrocarbon group having 1 to 10 carbon atoms, a group $-Si(R^9)_3$, or a group $-SO_3R^{10}$, n12 represents an integer from 1 to 3, q represents an integer from 0 to 9, provided that, when two or more R^{14}s exist, the R^{14}s may be the same or different, and R^9 and R^{10} represent alkyl groups having 1 to 10 carbon atoms.

4. The immersion exposure liquid according to claim 3, wherein the compound of the formula (1-1) is shown by the following formula (2-1), and the compound of the formula (1-4) is shown by the following formula (2-2),



(2-1) (2-2)

wherein, in the formula (2-1), R^1 represents an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a cyano group, a hydroxyl group, a fluorine atom, a fluorine-substituted hydrocarbon group having 1 to 10 carbon atoms, a group $-Si(R^9)_3$, or a group $-SO_3R^{10}$, a represents an integer from 0 to 10, provided that, when two or more R^1s exist, the R^1s may be the

same or different, and two or more R^1s may be bonded to form a ring structure, and R^9 and R^{10} represent alkyl groups having 1 to 10 carbon atoms, and, in the formula (2-2), R^5 represents an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a cyano group, a hydroxyl group, a fluorine atom, a fluorine-substituted hydrocarbon group having 1 to 10 carbon atoms, a group $-Si(R^9)_3$, or a group $-SO_3R^{10}$, i represents an integer from 0 to 2, provided that, when two or more R^5s exist, the R^5s may be the same or different, and two or more R^5s may be bonded to form a ring structure, and R^9 and R^{10} represent alkyl groups having 1 to 10 carbon atoms.

5. The immersion exposure liquid according to claim 1, wherein, when contacting the liquid with a photoresist film for 180 seconds in a nitrogen atmosphere so that the liquid film has a thickness of 1 mm, the liquid shows a change in absorbance of light with a wavelength of 193 nm of 0.05 or less before and after the contact at an optical path length of 1 cm.

6. The immersion exposure liquid according to claim 1, wherein the immersion exposure liquid contains the alicyclic hydrocarbon compound or the cyclic hydrocarbon compound containing a silicon atom in its ring structure in an amount of 95 wt% or more of the immersion exposure liquid.

7. The immersion exposure liquid according to claim 1, wherein the immersion exposure liquid has a dissolved oxygen content of 2 ppm or less.

8. The immersion exposure liquid according to claim 1, wherein the immersion exposure liquid has a total metal content of 10 ppb or less.

9. The immersion exposure liquid according to claim 8, wherein the metal is at least one metal selected from lithium, sodium, potassium, magnesium, copper, calcium, aluminum, iron, zinc, and nickel.

10. The immersion exposure liquid according to claim 1, wherein the immersion exposure liquid has a viscosity of 0.01 Pa·s or less at 25°C.

11. The immersion exposure liquid according to claim 1, wherein the immersion exposure liquid has a refractive index of 1.63 or more at a wavelength of 193 nm.

12. The immersion exposure liquid according to claim 11, wherein the immersion exposure liquid has a transmittance of radiation with a wavelength of 193 nm of 95% or more at an optical path length of 1 mm.

13. The immersion exposure liquid according to claim 4, wherein the compound of the formula (2-1) is trans-decahydronaphthalene, and the immersion exposure liquid has a transmittance of radiation with a wavelength of 193 nm of 95% or more at an optical path length of 1 mm and a dissolved oxygen content of 2 ppm or less.

14. The immersion exposure liquid according to claim 13, wherein the immersion exposure liquid is a liquid with a purity of 95 wt% or more which is obtained by subjecting a trans-decahydronaphthalene raw material to washing with concentrated sulfuric acid and distillation in a nitrogen atmosphere.

15. The immersion exposure liquid according to claim 4, wherein the compound of the formula (2-2) is exo-tetrahydrodicyclopentadiene, and the immersion exposure liquid has a transmittance of radiation with a wavelength of 193 nm of 95% or more at

an optical path length of 1 mm and a dissolved oxygen content of 2 ppm or less.

16. The immersion exposure liquid according to claim 15, wherein the immersion exposure liquid is a liquid with a purity of 95 wt% or more which is obtained by subjecting an exo-tetrahydrodicyclopentadiene raw material to washing with concentrated sulfuric acid and distillation in a nitrogen atmosphere.

17. A method of producing the immersion exposure liquid according to claim 1, the method comprising subjecting the liquid comprising the alicyclic hydrocarbon compound or the cyclic hydrocarbon compound containing a silicon atom in the ring structure to at least one of washing with concentrated sulfuric acid and distillation in a nitrogen atmosphere.

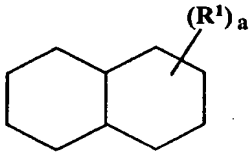
18. An immersion exposure method comprising applying an exposure beam to a mask and exposing a substrate using the exposure beam through a liquid provided between a lens of a projection optical system and the substrate, the liquid being the immersion exposure liquid according to claim 1.

19. The immersion exposure method according to claim 18, wherein an immersion upper layer film is formed on a surface of a resist film on the substrate, the immersion upper layer film containing a resin component which is soluble in an alkaline developer and insoluble in the immersion exposure liquid according to claim 1 and containing at least one of a hexafluorocarbinol group and a carboxyl group as a substituent for providing the alkali solubility.

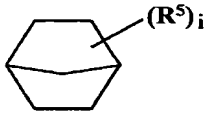
20. A method of evaluating the degree of contamination of an immersion exposure liquid during immersion exposure, the immersion exposure liquid being used for an

immersion exposure device or an immersion exposure method in which a substrate is exposed through a liquid provided between a lens of a projection optical system and the substrate, the method comprising contacting the immersion exposure liquid with a photoresist film formed on the substrate in a nitrogen atmosphere, and comparing absorbances of the liquid measured for light with a wavelength of 193 nm before and after the contact to evaluate the degree of contamination of the immersion exposure liquid.

21. A liquid composition comprising a compound of the following formula (2-1) or (2-2) in an amount of 95 wt% or more and having a dissolved oxygen content of 2 ppm or less,



(2-1)



(2-2)

wherein, in the formula (2-1), R^1 represents an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a cyano group, a hydroxyl group, a fluorine atom, a fluorine-substituted hydrocarbon group having 1 to 10 carbon atoms, a group $-Si(R^9)_3$, or a group $-SO_3R^{10}$, a represents an integer from 0 to 10, provided that, when two or more R^1s exist, the R^1s may be the same or different, and two or more R^1s may be bonded to form a ring structure, and R^9 and R^{10} represent alkyl groups having 1 to 10 carbon atoms, and in the formula (2-2), R^5 represents an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group having 3 to 14 carbon atoms, a cyano group, a hydroxyl group, a fluorine atom, a fluorine-substituted hydrocarbon group having 1 to 10 carbon atoms, a group $-Si(R^9)_3$, or a group $-SO_3R^{10}$, i represents an integer from 0 to 2, provided that,

when two or more R^5s exist, the R^5s may be the same or different, and two or more R^5s may be bonded to form a ring structure, and R^9 and R^{10} represent alkyl groups having 1 to 10 carbon atoms.

22. The liquid composition according to claim 21, wherein the liquid composition has a total metal content of 10 ppb or less.

23. The liquid composition according to claim 21, wherein the compound of the formula (2-1) is trans-decahydronaphthalene, and the liquid composition has a transmittance of radiation with a wavelength of 193 nm of 95% or more at an optical path length of 1 mm.

24. The liquid composition according to claim 21, wherein the compound of the formula (2-2) is exo-tetrahydrodicyclopentadiene, and the liquid composition has a transmittance of radiation with a wavelength of 193 nm of 95% or more at an optical path length of 1 mm.

25. The liquid composition according to claim 21, wherein the compound of the formula (2-1) or (2-2) is purified by at least one of washing with concentrated sulfuric acid and distillation in a nitrogen atmosphere.